

OFFICE OF NAVAL RESEARCH  
END-OF-THE-YEAR REPORT  
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

GRANT: N00014-96-1-1056

PR Number 97PR0-6782-00

**Polymerized Phthalocyanines for Electrochemical Applications**

*Peter W. Faguy, Richard P. Baldwin and Robert M. Buchanan*

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August 4, 1997

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PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

PR Number: 97PR0-6782  
Contract/Grant Number: N00014-96-1-1056  
Contract/Grant Title: Polymerized Phthalocyanines for Electrochemical Applications  
Principal Investigator: Peter W. Faguy  
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- a. Number of papers submitted to refereed journals, but not published: 0
- b. Number of papers published in refereed journals (for each, provide a complete citation): 0
- c. Number of books or chapters submitted, but not yet published: 0
- d. Number of books or chapters published (for each, provide a complete citation): 0
- e. Number of printed technical reports/non-refereed papers (for each, provide a complete citation): 0
- f. Number of patents filed: 0
- g. Number of patents granted (for each, provide a complete citation): 0
- h. Number of invited presentations (for each, provide a complete citation): 4
- i. Number of submitted presentations (for each, provide a complete citation): 3
- j. Honors/Awards/Prizes for contract/grant employees (list attached): 0  
(This might include Scientific Society Awards/Offices, Selection as Editors, Promotions, Faculty Awards/Offices, etc.)
- k. Total number of Full-time equivalent Graduate Students and Post-Doctoral associates supported during this period, under this PR number: 1.167  
Graduate Students: 1.167  
Post-Doctoral Associates: 0  
including the number of,  
Female Graduate Students: 0.417  
Female Post-Doctoral Associates: 0  
the number of  
Minority Graduate Students: 0.5  
Minority Post-Doctoral Associates: 0  
and, the number of  
Asian Graduate Students: 0.667  
Asian Post-Doctoral Associates: 0
- l. Other funding (list agency, grant title, amount received this year, total amount, period of performance and a brief statement regarding the relationship of that research to your ONR grant)

ONR - AASERT Award F97 *Polymerized Phthalocyanines for Electrochemical Applications*

## h. Invited Presentations

P.W. Faguy, "New Electrocatalysts for Fuel Cell Applications", invited lecture; Department of Chemical Engineering, University of Louisville, Louisville, KY; March 13, 1997.

P.W. Faguy, "Polymerized Tetraaminophthalocyanines: New Electrocatalysts for Fuel Cells", invited lecture; Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada; March 17, 1997.

P.W. Faguy, "Fuel Cells and Batteries in Electric Cars: Research Challenges and Opportunities", invited lecture; Department of Chemistry, West State College of Georgia, Carrolton, GA; April 11, 1997.

J.E. Pavez, J.P. Shaw, F. Bailly, R.P. Baldwin, R.M. Buchanan and P.W. Faguy, "The Electrochemical Polymerization of Tetraaminophthalocyanines to Form Conducting Polymers", invited talk; presented at the Electrochemistry Symposium at the Canadian Society for Chemistry Meeting, Windsor, Canada; June 1-4, 1997.

## i. Submitted Presentations

M. Huang, P.W. Faguy, R.P. Baldwin, J. Shaw, J. Pavez, J. Wang, F. Bailly and R.M. Buchanan, "Electrocatalytic Properties of Poly-Co-Tetraaminophthalocyanine Modified Electrodes", presented at the 213<sup>th</sup> National ACS Meeting, San Francisco, CA; April 13, 1977, paper 286.

J. Pavez, J. Shaw, F. Bailly, R.P. Baldwin, R.M. Buchanan and P.W. Faguy, "Polymerized Phthalocyanines for Electrochemical Applications" presented at the 3rd Annual Kentucky EPSCoR Conference, Lexington, KY; May 5, 1997.

M. Huang, J. Pavez, J. Shaw, F. Bailly, R.P. Baldwin, R.M. Buchanan and P.W. Faguy, "Oxygen Reduction on Poly-Cobalt Tetraaminophthalocyanine-modified Electrodes", presented at the 191<sup>st</sup> Meeting of the Electrochemical Society, Montreal, Canada; May 8, 1997, Abstract #1096.

## k. Graduate Students and Post-doctoral Associates

Hanlin Nie, Ph.D. student; June 1, 1996 to July 31, 1996; 16.7% FY97 FTE.

Min Huang, Ph.D. student; August 1, 1996 to August 31, 1996; 8.3% FY97 FTE.

Jianping Wang, Ph.D. student; August 1, 1996 to December 31, 1996; 41.7 FY97 FTE.

Jorge Pavez, visiting graduate student, University of Santiago, Santiago, Chile.  
December 1, 1996 to May 31, 1997, 50% FY97 FTE.

## l. Other Funding

ONR - AASERT Award F97 *Polymerized Phthalocyanines for Electrochemical Applications*  
\$120,000 cumulative; 06/01/97 - 05/31/00

Where the present grant addresses the application and development of polymerizable phthalocyanines for the electrocatalytic reduction of molecular oxygen for fuel cells, the AASERT grant focuses on the same polymerizable macrocycles with application to electrocatalytic amelioration of environmental toxins and pollutants.

- a. Principal Investigator:** Peter W. Faguy
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- c. Cognizant ONR Program Officer:** Richard T. Carlin, Electrochemical Science and Technology, Chemistry and Physics, S&T Division

**d. Program Objective**

The main objective of our research program is to develop new electrode materials for oxygen reduction based on polymeric aminophthalocyanines, poly-MTAPc's. Reaching this objective depends on successful outcomes in the following endeavors:

- optimization of monomer syntheses, of polymer formation, and of transition metal exchange in the polymer;
- characterization of O<sub>2</sub> reduction at poly-MTAPC-modified electrodes, in terms of both mechanism and kinetics;
- description, at a molecular level, of the polymer film based on electroanalytical and spectroscopic studies.

**e. Significant Results**

A new metal-free phthalocyanine, tertakisamino-phthalocyanine (H<sub>2</sub>TAPc), has been synthesized and metallated successfully with Co<sup>2+</sup>. The TAPc monomers have been characterized by a variety of electrochemical and spectroscopic techniques. The redox properties of dissolved, adsorbed and polymerized films of H<sub>2</sub>TAPc and CoTAPc have been studied in non-aqueous (DMF and DMSO) and aqueous solutions. Both of these monomers electropolymerize on ITO, Pt and GC electrodes in DMF and DMSO at ~+0.8 V vs. Ag/AgCl. Films polymerized from H<sub>2</sub>TAPc can be metallated by electrochemical cycling in DMSO (0.1 M TBAP) containing CoCl<sub>2</sub>. Poly-H<sub>2</sub>TAPc films catalyze hydrogen evolution with onset near -0.8 V in acidic solutions. Poly-CoTAPc modified electrodes reduce molecular oxygen with an onset potential of +0.2 V vs. Ag/AgCl in 0.05 M H<sub>2</sub>SO<sub>4</sub> and with no loss of activity over thousands of cycles. O<sub>2</sub> reduction is also electrocatalyzed in basic solution, again with no apparent loss of activity. In preliminary experiments, the films have retain their activity in the presence of methanol and chloride ion.

**f. Work Plan 1997 - 1998**

With respect our program goals and our 96/97 accomplishments, there are several obvious short-term objectives:

- 1) confirm the proposed kinetics and mechanism for  $O_2$  reduction on poly-CoTAPc-modified electrodes using rotating ring-disc hydrodynamic studies (underway);
- 2) demonstrate generality of electrochemically induced central metal exchange process ( $Ni^{2+}$  and  $Fe^{2+}$  studies underway);
- 3) quantify the extent of stability for poly-CoTAPc-modified electrodes toward methanol and chloride ion and for long cycle times, under real PEM fuel cell conditions.

Other objectives which will be addressed in the next year (and possibly extend into the following year), which involve more complicated experimental design and procedures include:

- 4) establish the mechanism of electrochemical polymer film formation using electrochemical methods and hybrid *in situ* techniques such as FTIR, Raman and QCM;
- 5) optimize film formation with respect to electrode performance and stability and in terms of fabrication methodology (e.g.; polymerization conditions: cycling / potentiostatic / galvanostatic, anion composition, solvent, etc.);
- 6) initiate studies into poly-FeTAPc-modified electrodes for oxygen reduction.

**g. Current Graduate Students**

Francois Bailly: M.Sc. expected September, 1998.

Pablo Condes: Ph.D. expected 2001.

Jorge Pavez: Ph.D. (University of Santiago), leaving project December, 1997.

William Todd: pre-M.Sc. student, leaving project December, 1997.

# Polymerized Phthalocyanines for Electrochemical Applications

Faguy/Baldwin/Buchanan, University of Louisville

**Technology Issues:** Fuel cells which employ transition metal macrocycles as O<sub>2</sub> electrocatalysts demonstrate less than optimal performance due to loss of activity and/or poisoning; new electrode materials are needed.

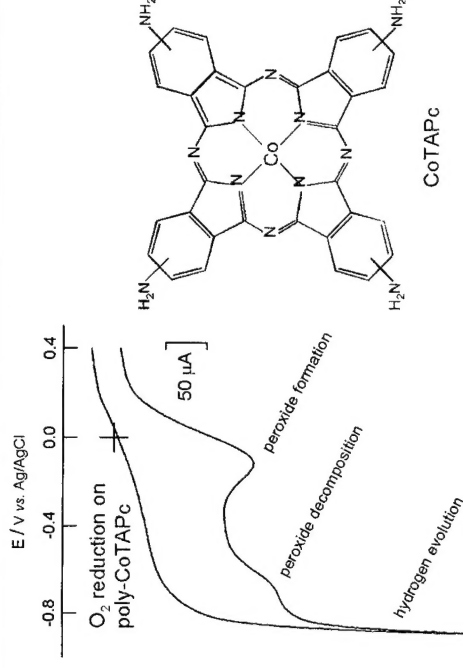
**Objective:** Develop new polymeric macrocyclic electrocatalysts which demonstrate a 4 e<sup>-</sup> reduction pathway, low overpotentials and long-term stability.

## Approach:

- Modify existing synthetic routes to prepare various tetraaminophthalocyanines.
- Develop novel metallation methods to make MTAPc's.
- Optimize the electro-oxidation process leading to polymer film formation.
- Study O<sub>2</sub> reduction kinetics at poly-MTAPc-modified electrodes.
- Characterize the polymer films using electroanalytical and spectroscopic methods.

## Accomplishments:

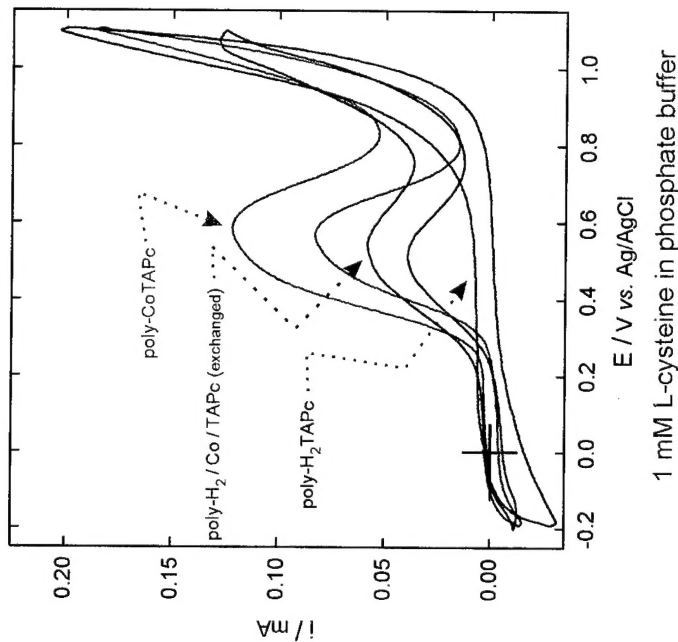
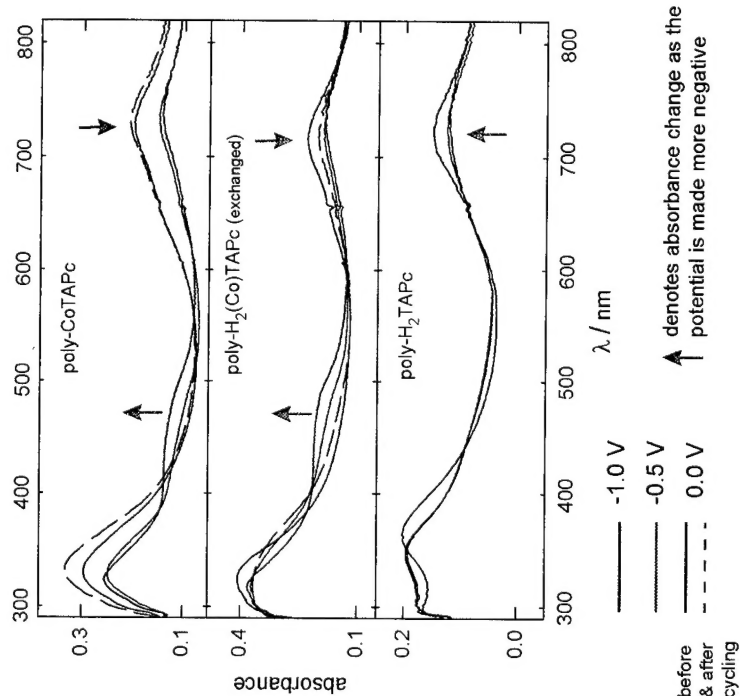
- Demonstrated a novel route to poly-CoTAPc films via electrochemical exchange of Co<sup>2+</sup> in the poly-H<sub>2</sub>TAPc film.
- Achieved facile O<sub>2</sub> reduction at poly-MTAPc films:
 
$$\begin{aligned} M=H_2 &\rightarrow 2 e^- \\ M=Mg &\rightarrow 2 e^- \\ M=Co &\rightarrow 4 e^- \quad (2+2) \end{aligned}$$
- Demonstrated long-term stability for poly-CoTAPc films as O<sub>2</sub> reduction catalysts.



## Impact:

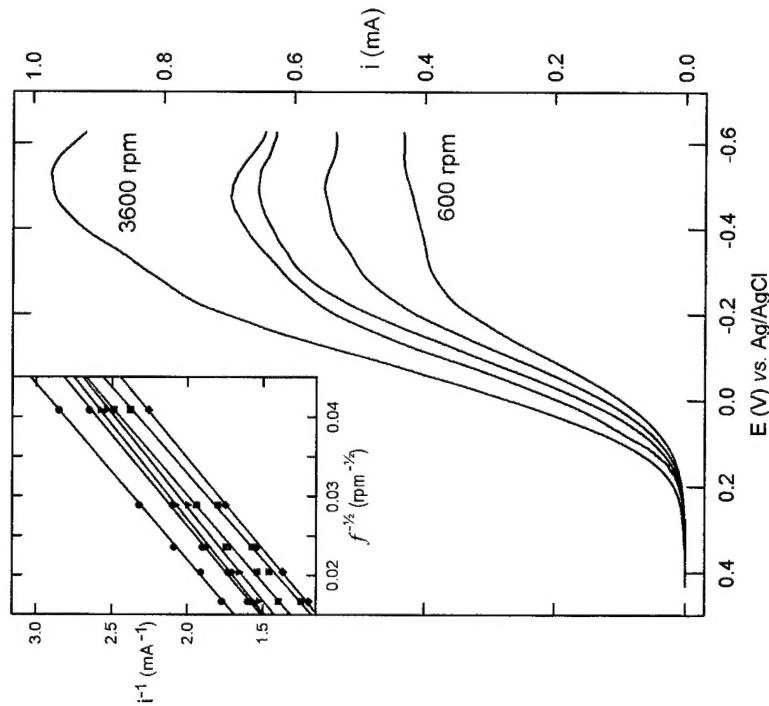
- New poly-TAPc-based O<sub>2</sub> reduction catalysts, demonstrating stability and performance, predict a new chapter for research into macrocyclic fuel cell catalysts.
- Exciting possibilities for transition metal and non-transition metal hybrid poly-M, M' TAPc films for electrocatalysis and electroanalysis now exist.

## electrochemically induced metallation of poly-H<sub>2</sub>TAPc films



**Accomplishment & Impact:** No previous demonstration of an electrochemically induced metallation for a macrocycle-modified electrode exists. UV-visible spectroelectrochemistry (LH panel) and electrocatalysis (RH panel) confirm that Co<sup>2+</sup> is being incorporated as the central cation in the TAPc macrocycle. From robust, easily formed poly-H<sub>2</sub>TAPc films, a wide variety of transition metal and mixed metal electrocatalysts could be made. Regeneration of active transition metal centers could be possible for fuel cell electrodes, and for electroanalytical and electrochemical remediation applications.

## ***4e<sup>-</sup> reduction of O<sub>2</sub> on poly-CoTAPc films***



O<sub>2</sub> reduction RDE study in 0.05 M H<sub>2</sub>SO<sub>4</sub>

for -220 mV > E > -380 mV (higher  $\eta$  region):

- all lines parallel ( $r^2$  values > 0.990) ➔ reaction is 1<sup>st</sup> order with respect to O<sub>2</sub>
- slope<sup>-1</sup> =  $\beta$  (Levich parameter) ➔ 0.021 <  $\beta$  < 0.028
- $\bar{\beta} = 0.023 \text{ mA}/(\text{rpm})^{1/2}$  4e<sup>-</sup> process

**Accomplishments & Impact:** The work to date has indicated that poly-CoTAPc films electrocatalyze the four electron reduction of oxygen to water in acidic media and to OH<sup>-</sup> in basic media. The mechanism most probably involves two sequential 2e<sup>-</sup> reductions. The onset potential for O<sub>2</sub> reduction, the behavior at high rotation rates, and the robustness of the film towards electrochemical cycling all reflect favorably on the potential of these novel polymeric films for fuel cell applications. The film stability is present in acidic and basic solutions. Furthermore, oxygen reduction on poly-CoTAPc-modified electrodes is not adversely affected by the presence of either methanol or chloride ion in the electrolyte solution.